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Combination of Chemical Ionization (CI) and Low Energy Ionization Capabilities with High-resolution Time-of-Flight GC/MS

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Introduction

Important applications for high-resolution gas chromatography mass spectrometer (GC/MS) systems include untargeted screening approaches as well as unknown compound identification. For many classes of compounds, low energy electron ionization (EI) provides significant improvements in the relative abundance of molecular ions as compared to standard (70 eV) EI, and thus enables enhancement in selectivity and compound identification capability without any down time due to changing the ion source or additional tuning. However, there is still an opportunity for alternative ionization sources as a complimentary technique (i.e., chemical ionization), combined with high resolution GC/MS, as will be demonstrated here for selected compounds predominantly of environmental significance.

Experimental

All experiments were performed using an Agilent 7890B GC system coupled to a high resolution 7250 GC/Q-TOF equipped with a low energy capable EI source and an interchangeable prototype CI source. The data were collected in both EI as well as positive (PCI) and negative (NCI) modes with methane as a reagent gas. Selected groups of compounds included chlorinated phenols, nitroaromatics and pesticides among others.

Typical MS parameters are listed in Table 1.

The GC separation was done on a 30 m x 0.25 mm id x 0.25 µm film thickness HP-5MS capillary column using He as carrier gas at 1.2 mL/min. The injector temperature and the MS interface were set at 280ºC Methane (99.995%) was used as reagent gas. For positive CI the methane flow was set at 20% and for negative CI at 40%. For NCI, the source and the quadrupole temperatures were set at 150ºC. For PCI, the source temperature was set at 280ºC and the quadrupole temperature at 150ºC. The spectral data were acquired at 5 Hz and the mass range was 50-1200 m/z. 2H-Perfluoro-5,8-dimethyl-3,6,9-trioxa-dodecane (PFDTD) was used to tune the mass spectrometer in the CI mode.

Data analysis was performed using Agilent MassHunter Qualitative Analysis software version B.08 as well as MassHunter Quantitative Analysis software version B.09.

Experimental

Ionization mode	Standard EI	Low Energy EI	Positive CI	Negative CI
Electron energy, eV	70	9-17	110	70-200
Emission current, µA	5	0.3-1	150	50-130
Source temperature, °C	200-280	200	280	150
Mass range, m/z	50-1200			
Spectral acquisition rate	5 Hz			

Table 1. GC/Q-TOF MS Acquisition Parameters. The source temperature was chosen separately for each experiment based on the compound group and ionization mode. Emission current was optimized for each electron energy.

LOD for both negative and positive CI were statistically derived based on repetitive injections of benzophenone and octofluoronaphthalene (OFN), respectively. In the positive CI mode LOD was calculated based on 10 pg/µL benzophenone injections and was estimated to be 3.4 pg on column. For NCI, LOD was calculated based on the injections of 10 fg/µL and 1 fg/µL OFN and was estimated to be 2.3 and 0.5 fg on column, respectively. Examples of EIC for OFN are shown in Figure 1.

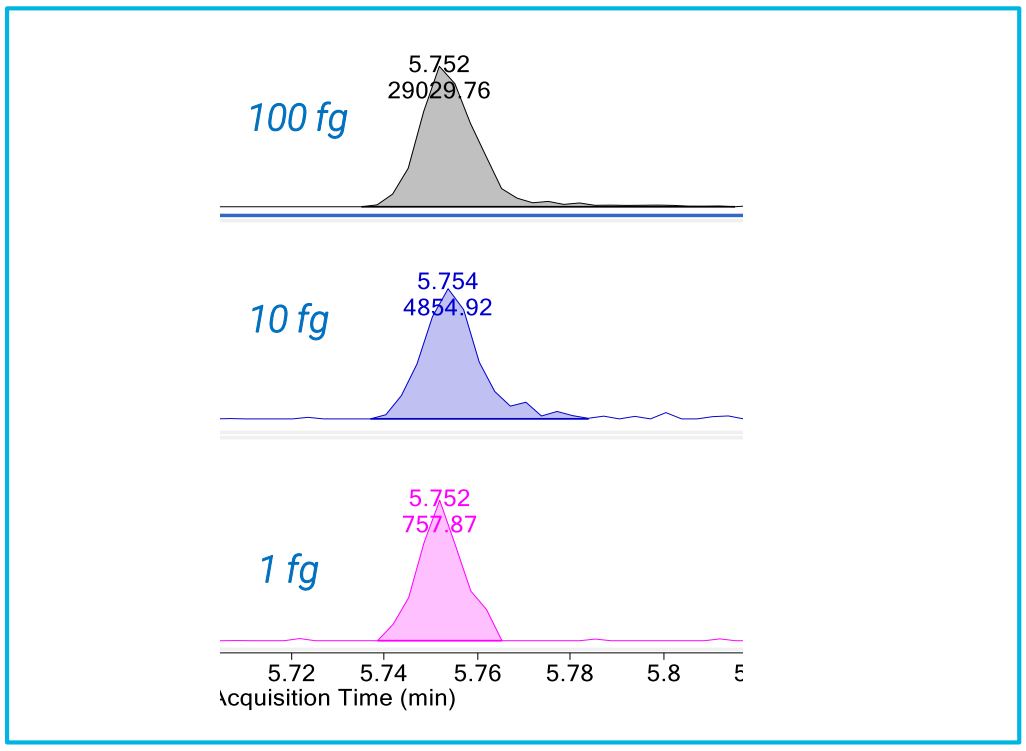

Figure 1. EIC for the molecular ion of OFN (1-100 fg on column) in NCI, 271.9878 +/- 20 ppm

Low electron energy-capable EI vs Positive CI

The interchangeable prototype CI source functionality was evaluated with traditional positive and negative CI checkout compounds to confirm fundamental CI performance. Next, fragmentation patterns of different compound classes of interest were compared between EI (standard, 70 eV; as well as low energy) and CI modes (Figure 2).

While some compounds form a significant (M+H)+ ion as well as methane adducts in PCI, others showed higher degrees of fragmentation in PCI as compared to low energy EI (Figure 2).

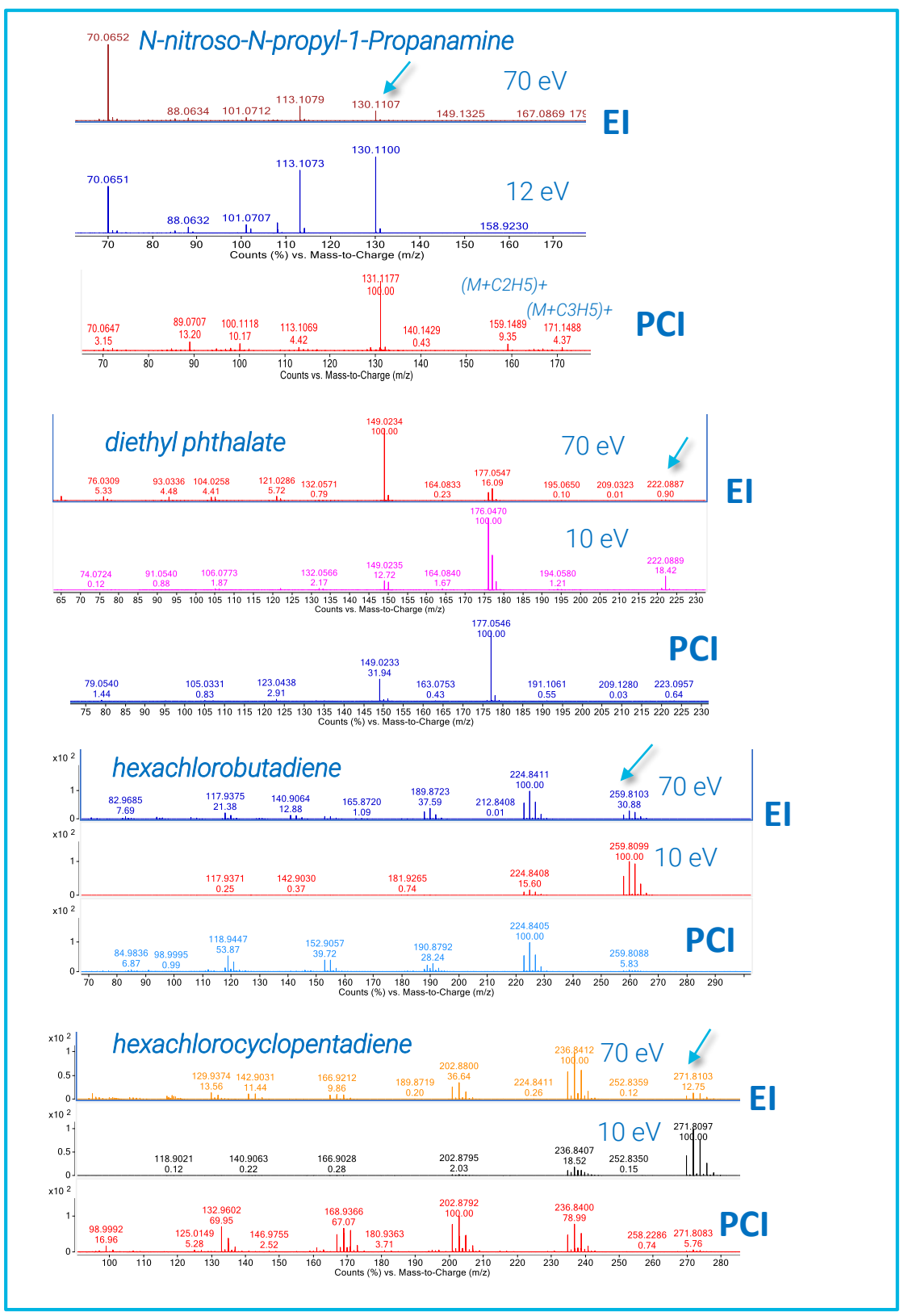

Figure 2. Fragmentation examples of spectra obtained in standard and low energy EI and compared to PCI. Arrow points to the molecular ion.

Negative CI

Negative CI was found to be particularly sensitive and selective for organophosphate, organochlorine and pyrethroid pesticides.

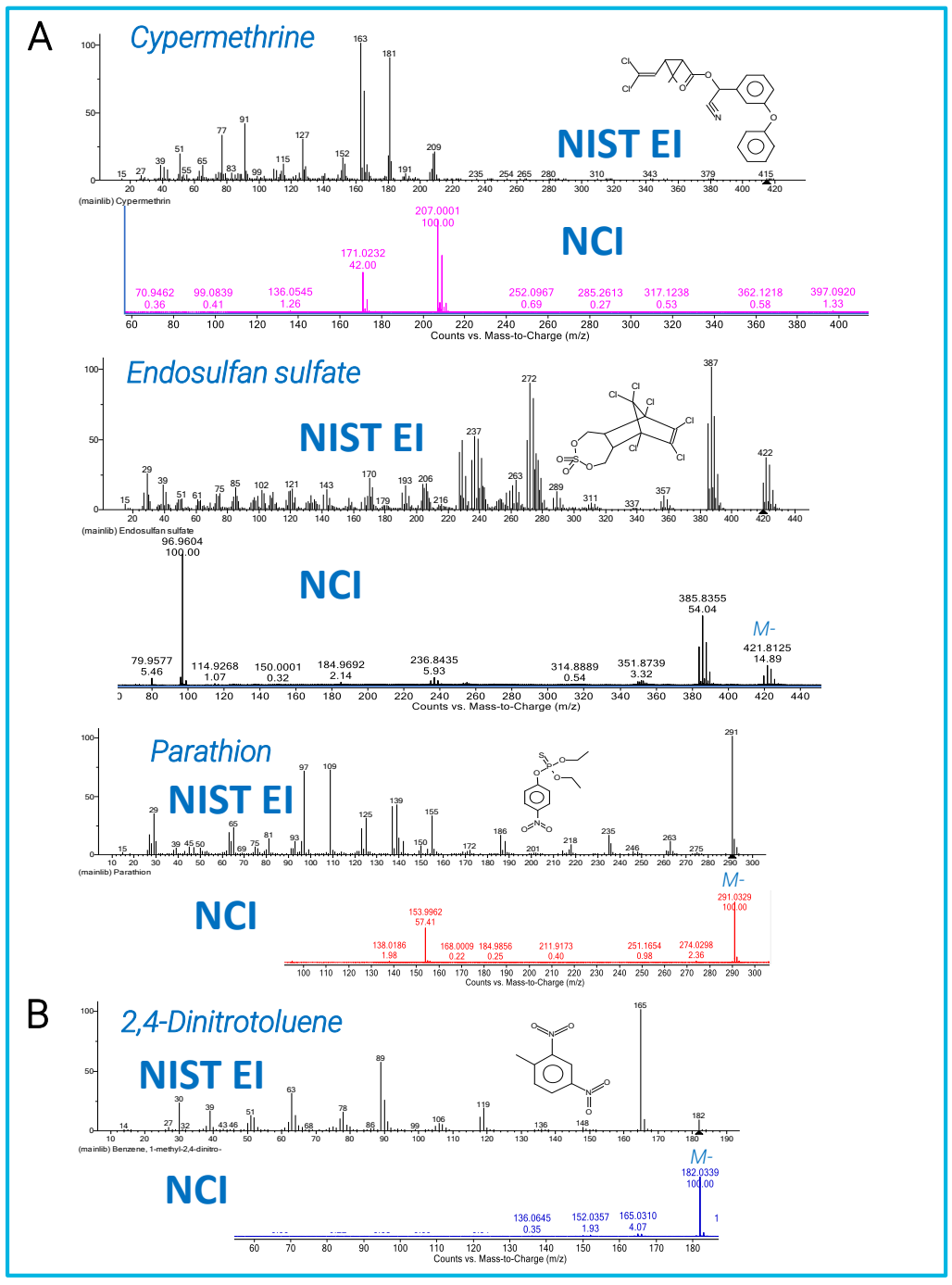

Figure 3. a) Significant decrease in the fragmentation with a concentration of the relative abundance in the molecular ion or characteristic fragment ions is typically observed for pyrethroid, organochlorine and organophosphate pesticides. b) This trend is also typical for nitroaromatic compounds.

Compound name	LOD, pg	Compound name	LOD, pg	Compound name	LOD, pg
Trifluralin	1.6	*Aldrin*	1.4	*Dieldrin*	1.4
Dicloran	1.1	*Chlorpyrifos*	1.2	*Ethion*	1.2
BHC-gamma (Lindane)	1.6	*Parathion*	1.2	*Endosulfan sulfate*	1.4
Fonofos	0.9	*Pendimethalin*	1.4	*Bifenthrin*	1.4
Tefluthrin	1.1	*Heptachlor exo-epoxide isomer B*	1.3	*Tetradifon*	1.0
Parathion-methyl	1.7	*Chlorfenvinphos*	1.6	*Phosalone*	1.5
Chlorpyrifos-methyl	1.7	*Methidathion*	2.9	*Cyhalothrin (lambda)*	1.3
Heptachlor	1.4	*Tetrachlorvinphos*	1.9	*Pyrazophos*	2.4
Fenitrothion	1.5	*Endosulfan*	1.1	*Cypermethrin I*	2.8
Malathion	1.3	*Prothiofos*	1.4	*Flucythrinate I*	1.0

Table 2. LOD for pesticides analyzed in NCI spiked to the broccoli extract. Injection volume 1 µl.

Results and Discussion

Identification of cis vs trans stereoisomers of various conazoles

Stereoisomers of etaconazole, propiconazole, difenoconazole were investigated using negative CI. These compounds have two chiral centers at the 2- and 4-positions on the dioxolane ring existing as two pairs of diastereoisomers (cis and trans), and two pairs of enantiomers that require chiral columns for separation.

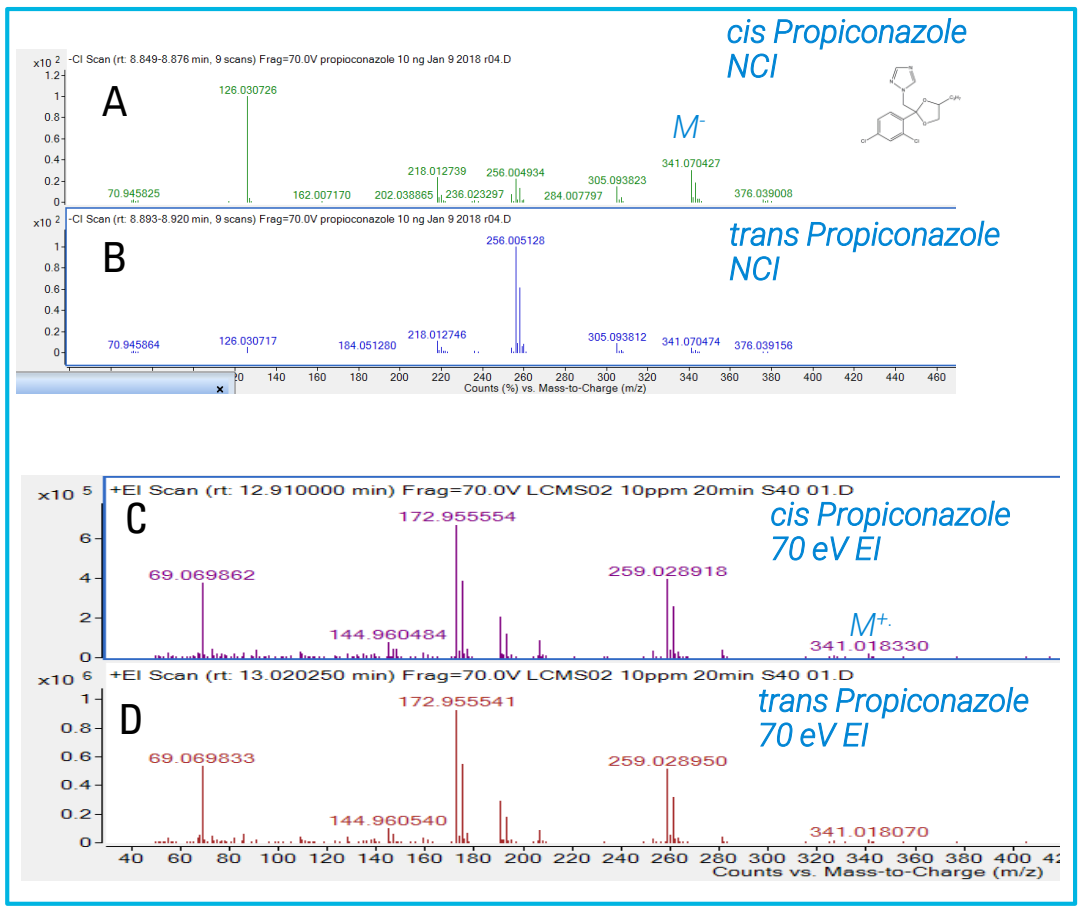

Figure 4. NCI spectra of cis and trans propiconazole (A and B) and the EI spectra of the same cis and trans stereoisomers (C and D).

As shown in Figure 4, NCI has a different fragmentation mechanism than EI. The EI mechanism is via elimination of the triazole ring ($C_3H_4N_3$) to form a stable tertiary ion at m/z 259.0289 ($C_{12}H_{13}O_2Cl_2$), followed by the opening of the 1,3-dioxolane ring and elimination of the side chain to form an abundant ion at m/z 172.9555 ($C_7H_3OCl_2$). In contrast, the NCI spectra of the cis and trans isomers are quite different making it possible to uniquely identify them. For the cis isomers, the most abundant peak in the spectra of eta- and propiconazole is the ion at m/z 126.0309 ($C_4H_4N_3O_2$) corresponding to the elimination of the dichlorophenyl group as well as the side chain including the carbons 4 and 5 on the 1,3- dioxolane ring.

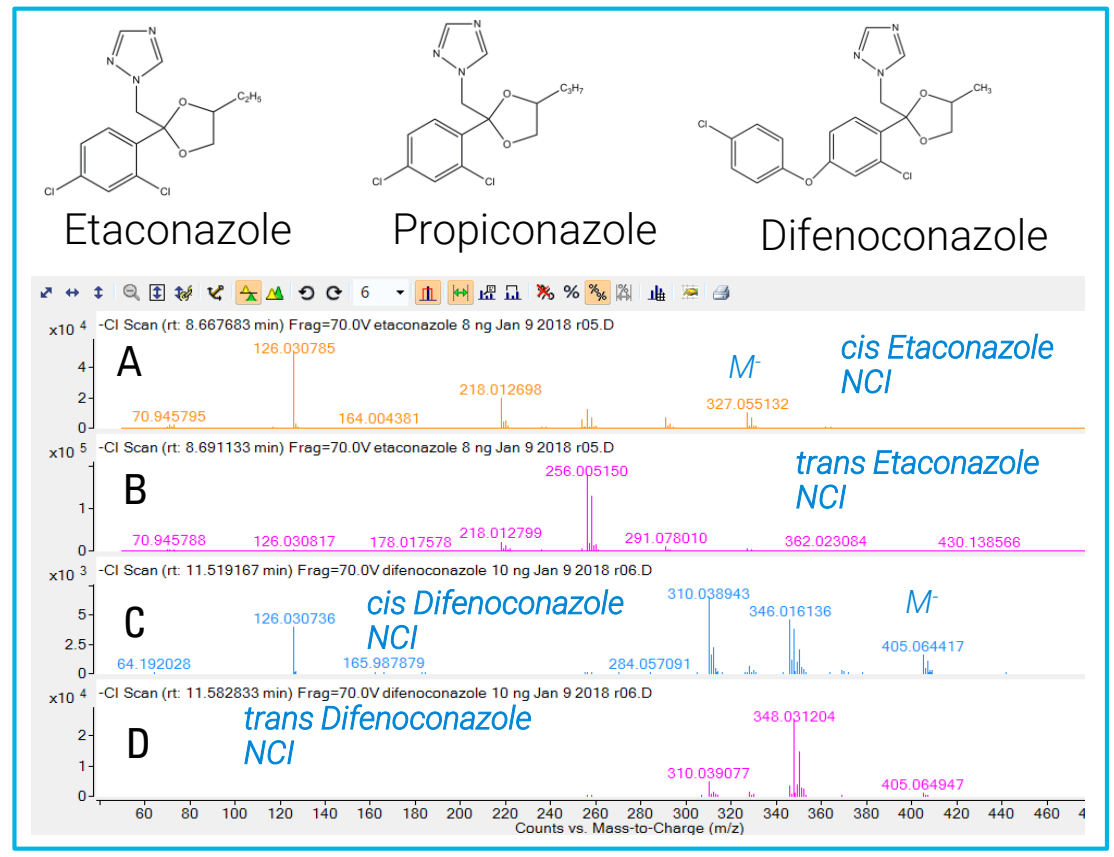

Figure 5. NCI spectra of cis and trans etaconazole (A and B) and difenoconazole (C and D).

The presence of the phenoxy group in the cis difenoconazole stabilizes the molecular ion somewhat, thus leading to the formation of the fragment ion at m/z 310.038943 ($C_{16}H_9N_3O_2Cl$). For the trans conazoles, the most abundant ions were at m/z 256.004991 ($C_{10}H_8N_3OCl_2$) for eta- and propiconazole, and m/z 348.031206 ($C_{16}H_{12}N_3O_2Cl_2$) for difenoconazole due to the additional phenoxy ring; these ions correspond to the elimination of the side chain attached to the 1,3-dioxolane ring. The mass accuracy and the % abundance of the molecular ions for the cis stereoisomers are given in Table 3. The relative abundances of the negative molecular ions (M-) for the trans stereoisomers are below 4%.

	cis		trans		M-	
	exp.m/z	mass error, ppm	exp.m/z	mass error, ppm	cis	% abundance
Etaconazole	126.030785	-0.9	256.00515	0.6	327.0551	20
Propiconazole	126.030726	-1.4	256.00513	0.5	341.0704	29
Difenoconazole	126.030736	-1.3	310.03894	0.2	405.0644	24

Table 3. Mass accuracy data for the cis – trans conazole stereoisomers and the % abundances of the molecular ions of the cis stereoisomers

Conclusions

- Benefits of the 7250 GC/Q-TOF system equipped with a low energy-capable EI source as well as an interchangeable prototype CI source were explored for targeted and untargeted analysis applications.
- Chemical ionization alone or in combination with low energy EI and a high-resolution GC/Q-TOF provides new opportunities in compound identification.

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